



Short communication

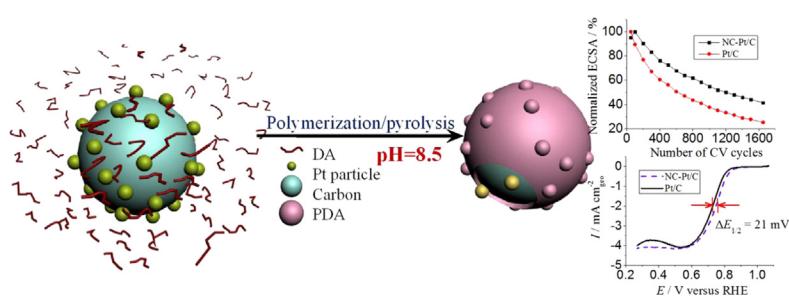
A bioinspired approach to protectively decorate platinum–carbon for enhanced activity and durability in oxygen reduction

Yiyin Huang ^{a, b}, Fang Fu ^{a, b}, Peng Wu ^{a, b}, Yaobing Wang ^{a, b, *}, Jiannian Yao ^c^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou 350002, PR China^b Key Laboratory of Design and Assembly of Functional Nanostructures, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou 350002, PR China^c Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

HIGHLIGHTS

- Pt/C was protectively decorated by DA self-polymerization and pyrolysis processes.
- Methanol tolerance of the NC–Pt/C catalyst was enhanced.
- NC–Pt/C still keeps 41.7% of its biggest ECSA after 1650 cycles.
- $E_{1/2}$ of NC–Pt/C for ORR was 21 mV more positive relative to Pt/C after cycles.
- Increased particle diameter in NC–Pt/C was markedly smaller than Pt/C after cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 March 2014

Received in revised form

18 June 2014

Accepted 18 June 2014

Available online 24 June 2014

Keywords:

Dopamine

Oxygen reduction

Platinum/carbon

Protective decoration

ABSTRACT

This work develops a versatile and effective approach of protective decoration to improve the catalytic performance of nanostructured catalysts. The commercial platinum–carbon catalyst is decorated with polydopamine carbide via self-polymerization and pyrolysis processes. The electrocatalytic performance of the novel polydopamine carbide decorated platinum–carbon catalyst is characterized by voltammogram. Origin of improvement in its performance is analyzed by X-ray photoelectron spectroscopy and transmission electron microscope. It is exhibited that the catalytic activity and durability for oxygen reduction reaction and methanol tolerance of the polydopamine carbide decorated platinum–carbon catalyst are enhanced. The promoted effects result from the thermal treatment and decoration of polydopamine carbide which provides N species, slightly alters the Pt electronic structure and prevents Pt from agglomeration during long-term potential cycling.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Carbon supported Pt (Pt/C) catalysts of the cathodes in direct methanol fuel cells (DMFCs) undergo dissolution and agglomeration during operation on account of low pH, high potential, high oxygen concentration and high relative humidity [1,2], bringing about decrease in Pt surface area and cathode catalytic efficiency [3]. One effective way to address this issue is decorating Pt/C with a

* Corresponding author. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou 350002, PR China. Tel./fax: +86 591 2285 3916.

E-mail address: wangyb@fjirsm.ac.cn (Y. Wang).

protectant (e.g., a polymer or an oxide). For example, Pt/C was decorated with nafion during synthesis [4] or with polyaniline by induced polymerization in the presence of ammonium peroxodisulfate at a low temperature (<5 °C) [5]. These two catalysts above exhibited enhanced stability after decoration. In order to drive organics to directionally polymerize and decorate the catalyst, reaction conditions need to be accurately controlled in many cases. Furthermore, many decorated noble metal catalysts were ignored to be assessed for their methanol tolerance [4–7]. However, this assessment is very important because cathode catalytic efficiency can also be decreased by methanol cross-over through proton exchange membrane (PEM) in DMFCs.

As a versatile adhesive in living nature, dopamine (DA) can very easily adhere to nearly all types of material surfaces via spontaneous adsorption and polymerization processes [8,9]. Formation of polydopamine (PDA) coating involves the step of oxidizing catechol to quinone, followed by polymerization in a sense reminiscent of melanin formation [9,10]. Owing to this versatile adhesive attraction, DA can be used to decorate Pt/C for enhanced stability. However, PDA is not absolutely stable in strongly acidic medium [9]. To

overcome this defect, PDA should be converted into N-doped carbon (NC, PDA carbide) [11] by its pyrolysis in inert atmosphere. In this work, a novel PDA carbide-decorated Pt/C catalyst was synthesized via self-polymerization and pyrolysis processes. Methanol tolerance, oxygen reduction reaction (ORR) activity and ORR catalytic durability of the NC–Pt/C catalyst were investigated.

2. Experimental

2.1. Synthesis of catalyst

The NC–Pt/C catalyst was synthesized by self-polymerization and pyrolysis processes of dopamine on the commercial Pt/C catalyst (20 wt%, Johnson Matthey). A typical preparation consisted of the following steps: 100 mg of the Pt/C catalyst and 25 mg of dopamine hydrochloride were dispersed in 100 and 40 ml of double distilled water under ultrasonic stirring, respectively. The dopamine hydrochloride solution was added dropwise to the Pt/C suspension above under magnetic stirring. After that, the pH of the mixture was adjusted to 8.5 by a 1.5 M of Tris–HCl solution.

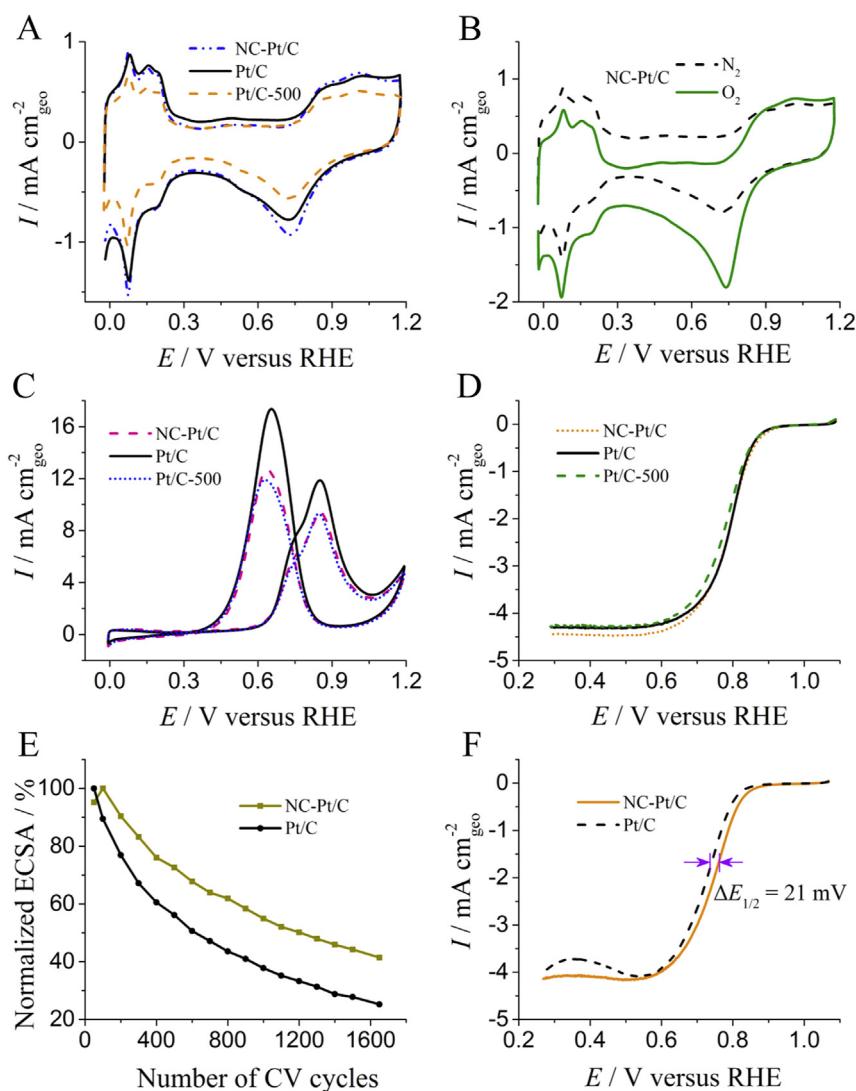


Fig. 1. (A) Cyclic voltammograms of Pt/C, Pt/C-500 and NC–Pt/C in N_2 -saturated 0.5 M H_2SO_4 ; (B) Cyclic voltammograms of NC–Pt/C in O_2 -saturated (solid lines) and N_2 -saturated 0.5 M H_2SO_4 (dash lines); (C) Cyclic voltammograms of Pt/C, Pt/C-500 and NC–Pt/C in 0.5 M H_2SO_4 + 1 M CH_3OH ; Rotating-disk voltammograms of the as-prepared catalysts in O_2 -saturated 0.5 M H_2SO_4 at 1600 rpm before (D) and after (F) 1650 CV cycles in N_2 -saturated 0.5 M H_2SO_4 ; (E) Normalized Pt ECSAs of the Pt/C and NC–Pt/C electrodes as functions of the number of CV cycles in N_2 -saturated 0.5 M H_2SO_4 . Cyclic voltammogram was conducted at 50 mV s⁻¹.

Dopamine molecules in the solution can self-adsorb and polymerize on the Pt/C surface and this reaction was conducted for 24 h under constant stirring. The mixture was filtered, washed and dried overnight. The final NC–Pt/C catalyst was obtained by carbonizing the residue in argon atmosphere at 500 °C for 4 h. For comparison, the commercial Pt/C catalyst was also thermally treated in the same condition and defined as Pt/C-500.

2.2. Physical and electrochemical characterization

The Pt loading of the NC–Pt/C catalyst was determined using an Ultima2 inductively coupled plasma OES spectrometer (ICP-OES, Jobin Yvon) and the value was 19.4 wt.%. The dispersed state as well as size distribution of the catalysts was characterized using a JEOL JEM-2010 transmission electron microscope (TEM) with a micro-analyser whose resolution power is 129 eV. The chemical valences of Pt and N in the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) with an Al K α X-ray source at 1487 eV. The chamber pressure was kept below 3×10^{-10} mbar during test. Specific correction was done by using a C 1s binding energy of 285 eV.

A CHI660e electrochemical working station (CH Instrument Inc.) was used to perform the electrochemical measurements. The mercury sulfate electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M H}_2\text{SO}_4$) was used as the reference electrode and all potentials in this work are given relative to the reversible hydrogen electrode (RHE). A Pt rod was used as the counter electrode. A glassy carbon (0.1963 cm^2) electrode covered by catalyst was used as the working electrode. For preparing the working electrode, a specific amount of the catalytic material was dispersed in a suspension of 50 μl of 20 wt.% Nafion solution (DuPont, USA) and 1950 μl of isopropyl alcohol by ultrasonic stirring. An aliquot of the slurry was spread on the polished glassy carbon electrode surface and the electrode was dried at room temperature for 30 min. The total Pt loading on the electrode is 4 μg . All electrochemical measurements were conducted at 30 °C. The electrodes were pretreated by cyclic voltammogram (CV) cycling at a scan rate of 50 mV s^{-1} for 100 cycles in order to achieve a stable electrochemical response. The ORR polarization curves were obtained in an O_2 -saturated 0.5 M H_2SO_4 solution at 5 mV s^{-1} as the rotation speed was 1600 rpm.

3. Results and discussion

Methanol tolerance and electrocatalytic ORR of the NC–Pt/C, Pt/C-500 and Pt/C catalysts were examined by CV and rotating-disk voltammogram. The test currents were normalized with respect to the electrode area. The lines in Fig. 1(A) demonstrate that NC–Pt/C displays the hydrogen adsorption/desorption peak ($0.0 \text{ V} < E < 0.3 \text{ V}$) similar to that of Pt/C, and both of them are significantly higher than that of Pt/C-500, signifying Pt active sites were still exposed to the solution after polydopamine carbide decoration and the polydopamine carbide can prevent Pt from agglomeration during thermal treatment. In Fig. 1(B), significantly enhanced reduction currents can be observed at the peak potential of ca. 0.74 V for NC–Pt/C in the O_2 -saturated compared to the N_2 -saturated solution, revealing ORR on the catalysts occurred. As described above that methanol tolerance of catalysts is one of the important properties for the cathodes in DMFCs, the catalysts were consequently tested by CV in a sulfuric acid and methanol solution. The forward peak currents of NC–Pt/C and Pt/C-500 are 9.3 and 9.1 mA cm^{-2} , both lower than that of Pt/C (11.9 mA cm^{-2}) in Fig. 1(C). Higher methanol tolerance of NC–Pt/C and Pt/C-500 relative to Pt/C might be ascribed to the change in surface state after thermal treatment. The ORR activities of NC–Pt/C, Pt/C-500 and Pt/C were examined by rotating-disk voltammogram in an

O_2 -saturated sulfuric acid solution, as shown in Fig. 1(D). We can see from the polarization curves that thermal treatment of Pt/C results in a negative shift in half-wave potential ($E_{1/2}$) for ORR. However, the decoration of polydopamine carbide on Pt/C enhanced the ORR because the half-wave potentials of NC–Pt/C and Pt/C are the same and the limiting current of NC–Pt/C reaches 4.45 mA cm^{-2} , a little bigger than that of Pt/C (4.29 mA cm^{-2}). Stability of the NC–Pt/C and Pt/C catalysts was investigated by a long-term CV cycle test in the N_2 -saturated sulfuric acid solution. The electrochemical surface area (ECSA) was calculated by measuring the Coulombic charge of desorption/adsorption peak area ($0.0 \text{ V} < E < 0.3 \text{ V}$) [12] and normalized to its biggest value during potential cycling. Evolution of the normalized ECSA with the cycle number was plotted in Fig. 1(E). Obviously, the NC–Pt/C catalyst exhibits higher electrochemically stable than the Pt/C catalyst because the former keeps 41.7% of its biggest ECSA, while the latter drops to 25.2% of its biggest ECSA. The ORR activities of the two catalysts decayed in varying degrees after 1650 cycles as shown in Fig. 1(F). Compared to Pt/C, the half-wave potential of NC–Pt/C is 21 mV more positive, indicating that NC–Pt/C has prominent durability improvement for ORR over Pt/C.

Successful polymerization of DA on the catalyst can be confirmed by the fact that 2.3 at.% of N was detected in NC–Pt/C while no N element was found in Pt/C from XPS analysis. The high-

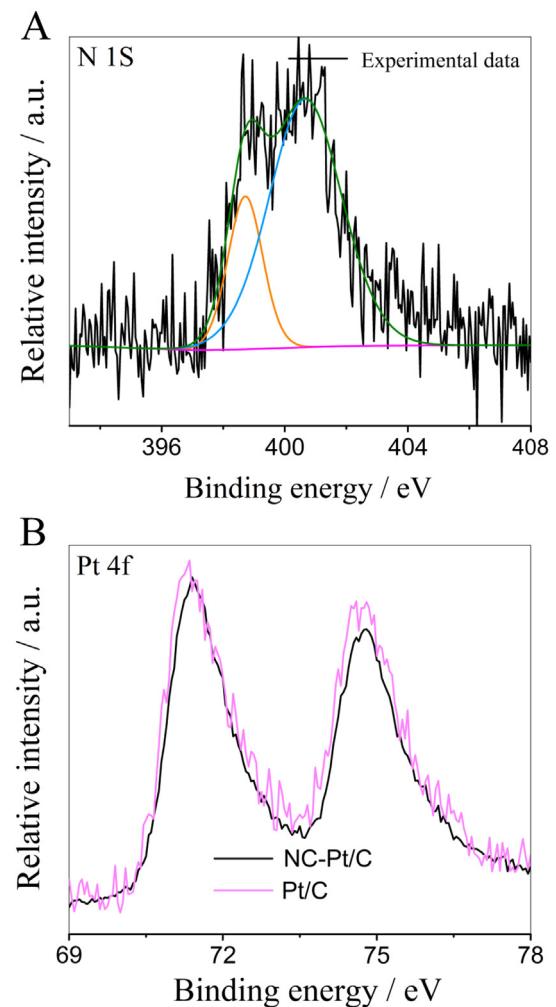


Fig. 2. (A) XPS spectrum of NC–Pt/C in N 1s region; (B) XPS spectra of NC–Pt/C and Pt/C in Pt 4f region.

resolution N 1s XPS spectrum of NC–Pt/C in Fig. 2 (A) is mainly identified into two component peaks at the binding energies (BEs) of 398.7 and 400.6 eV, corresponding to C–N and C=N [13,14], respectively, revealing the nitrogen existed in the carbon layer structure. The N 1s peak may contain some graphitic N species which is responsible for increase in the limiting current for ORR as shown in Fig. 1(D) and (F) [15]. The Pt 4f_{7/2} peak of NC–Pt/C shows a very slight shift to a higher binding energy (71.44 eV) compared to that of Pt/C (71.39 eV) in Fig. 2(B). This shift in binding energy is attributed to electron delocalization and partial ionization of Pt after NC decoration. This phenomenon may prevent formation of Pt–O bonds on NC–Pt/C to some extent and further alter the activity for ORR as demonstrated in Fig. 1(D) [4].

The dispersed state and particle size distribution of the NC–Pt/C and Pt/C catalysts before and after 1650 CV cycles are displayed in Fig. 3. Most Pt nanoparticles were uniformly dispersed on the carbon support surface. Particle size distribution was estimated by statistics of 1000 particles for each catalyst. As shown in Fig. 3(A) and (B), the average diameter of Pt nanoparticles is ca. 3.0 and 4.0 nm for Pt/C and NC–Pt/C, respectively. Thermal treatment of Pt/C induced sintering of Pt metal particles, which is also observed in Ref. [16]. It was shown that the specific activity of Pt particles for ORR increased in a sulfuric acid solution with the decreasing particle size from 5 to 1 nm [17]. However, the ORR activity of NC–Pt/C is a little higher than that of Pt/C in Fig. 1(D), suggesting that PDA carbide decoration gave an obvious promoting effect in ORR. After 1650 potential cycles,

the average diameter of Pt nanoparticles in Pt/C increases to 6.0 nm, while the value increases to 4.8 nm for NC–Pt/C. The smaller increment in diameter for NC–Pt/C indicates its better stability cycling in the sulfuric acid solution relative to Pt/C, which provides the basis for its better ORR durability as demonstrated in Fig. 1(F). Origin of this phenomenon can be attributed to protective decoration of Pt/C by PDA carbide which can prevent Pt from dissolution and agglomeration during cycling, similar to the protective mechanism of pod-like carbon nanotubes toward FeO_x [18].

4. Conclusions

The Pt/C catalyst was successfully decorated by PDA carbide via self-polymerization and pyrolysis processes. The protectively decorated PDA carbide not only provided N species and slightly altered the Pt electronic structure, but prevented Pt from dissolution and agglomeration in the acid solution. The inherent ORR activity as well as methanol tolerance of the NC–Pt/C catalyst was effectively enhanced. Structural stability and catalytic durability of NC–Pt/C for ORR were also greatly improved. The average diameter of Pt nanoparticles in the NC–Pt/C catalyst increased by 0.8 nm, lower than the value in Pt/C (3.0 nm) after long-term cycling. The half-wave potential of NC–Pt/C was 21 mV more positive compared to Pt/C after cycles. The excellent ORR performance together with high methanol tolerance makes the NC–Pt/C catalyst a better candidate for the application in the cathodes of DMFCs.

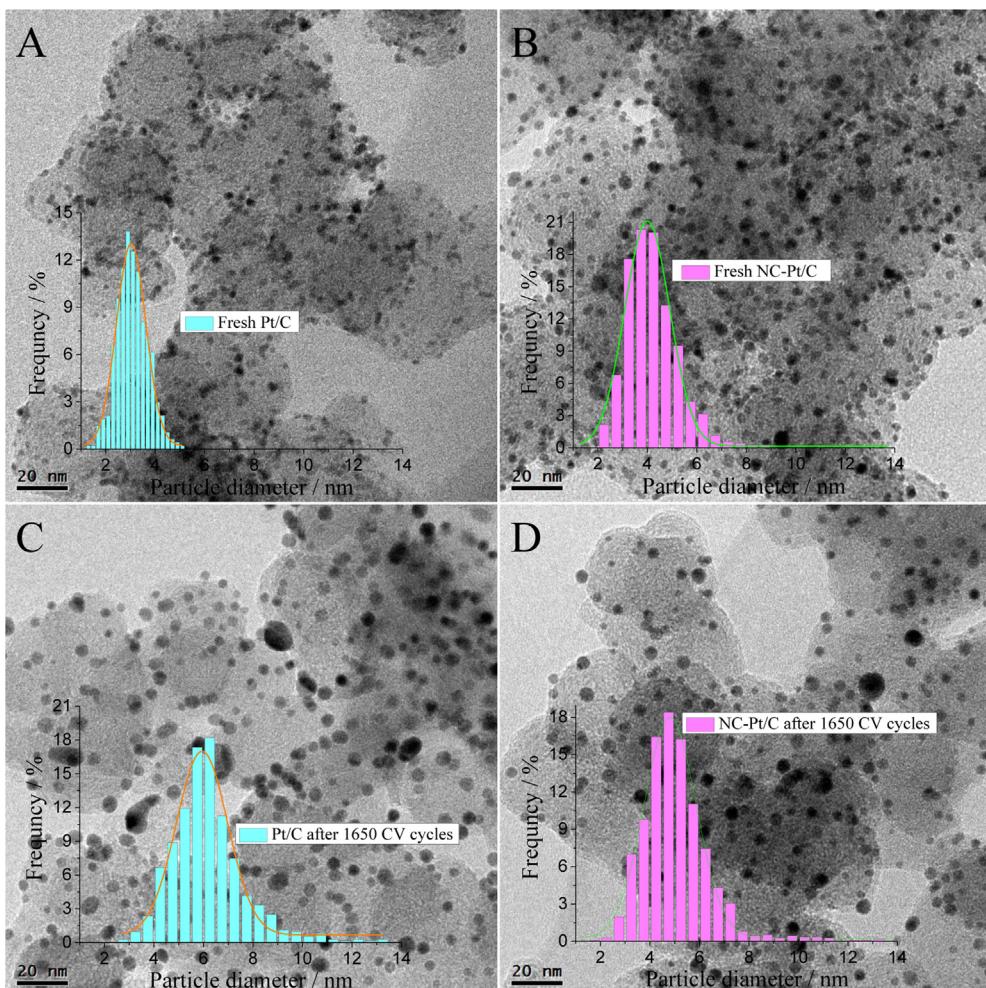


Fig. 3. The TEM images and the corresponding particle size distribution of Pt/C (A,C) and NC–Pt/C (B,D) before (A,B) and after (C,D) 1650 cycles in the 0.5 M H₂SO₄ solution.

Acknowledgments

This work was financially supported by the One Hundred Talents Program of the Chinese Academy of Sciences, the National Natural Science Foundation of China (No. 51342009) and the Natural Science Foundation of Fujian Province (No. 2014J05027).

References

- [1] J. Wang, G. Yin, Y. Shao, S. Zhang, Z. Wang, Y. Gao, *J. Power Sources* 171 (2007) 331–339.
- [2] S. Takenaka, H. Matsumori, H. Matsune, E. Tanabe, M. Kishida, *J. Electrochem. Soc.* 155 (2008) B929–B936.
- [3] S.Y. Huang, P. Ganeshan, B.N. Popov, *Appl. Catal. B Environ.* 102 (2011) 71–77.
- [4] S. Chen, Z. Wei, X.Q. Qi, L. Dong, Y.G. Guo, L. Wan, Z. Shao, L. Li, *J. Am. Chem. Soc.* 134 (2012) 13252–13255.
- [5] O.J. Curnick, P.M. Mendes, B.G. Pollet, *Electrochem. Commun.* 12 (2010) 1017–1020.
- [6] Y. Zhang, Q. Huang, Z. Zou, J. Yang, W. Vogel, H. Yang, *J. Phys. Chem. C* 114 (2010) 6860–6868.
- [7] C.W. Liu, Y.C. Wei, K.W. Wang, *Chem. Commun.* 46 (2010) 2483–2485.
- [8] L. Zhang, J. Wu, Y. Wang, Y. Long, N. Zhao, J. Xu, *J. Am. Chem. Soc.* 134 (2012) 9879–9881.
- [9] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science* 318 (2007) 426–430.
- [10] K.Y. Ju, Y. Lee, S. Lee, S.B. Park, J.K. Lee, *Biomacromolecules* 12 (2011) 625–632.
- [11] C. Lei, F. Han, D. Li, W.C. Li, Q. Sun, X.Q. Zhang, A.H. Lu, *Nanoscale* 5 (2013) 1168–1175.
- [12] Y. Huang, J. Cai, Y. Guo, *Int. J. Hydrogen Energy* 38 (2013) 3250–3256.
- [13] Y. Ma, C. Zhang, G. Ji, J.Y. Lee, *J. Mater. Chem.* 22 (2012) 7845–7850.
- [14] L. Zhao, Y.S. Hu, H. Li, Z.X. Wang, L.Q. Chen, *Adv. Mater.* 23 (2011) 1385–1388.
- [15] L. Lai, J. Potts, D. Zhan, L. Wang, C.K. Poh, C. Tang, H. Gong, Z. Shen, J. Lin, R. Ruoff, *Energy Environ. Sci.* 5 (2012) 7936–7942.
- [16] S. Brimaud, C. Coutanceau, E. Garnier, J.-M. Léger, F. Gérard, S. Pronier, M. Leoni, *J. Electroanal. Chem.* 602 (2007) 226–236.
- [17] M. Nesselberger, S. Ashton, J.C. Meier, I. Katsounaros, K.J.J. Mayrhofer, M. Arenz, *J. Am. Chem. Soc.* 133 (2011) 17428–17433.
- [18] D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, X. Bao, *Angew. Chem. Int. Ed.* 52 (2013) 371–375.